**Interpreting XPS and CV data from an Electrocatalysis Publication**

Based on: “Nickel-Iron Oxyhydroxide Oxygen-Evolution Electrocatalysts: The Role of Intentional and Incidental Iron Incorporation”, Lena Trotochaud, Samantha L. Young, James K. Ranney, and Shannon W. Boettcher, J. Am. Chem. Soc., 2014, 136, 6744–6753.

http://pubs.acs.org/doi/abs/10.1021/ja502379c

Before coming to class, read the entire article and answer the following questions, with special attention to Figure 1.

1. Please answer the following questions pertaining to the compiled XPS spectra in Figure 1(a).

1. Why was XPS chosen as a technique to study Fe content in the Ni-based thin films?

*XPS is an element-specific technique, so Fe content can be measured without interference from Ni or other elements that are present in the sample.*

1. From which orbital are photoelectrons ejected in the top XPS spectrum shown in Fig. 1(a)?

*In this particular experiment, electrons are ejected from 2p orbitals in Fe.  (At different X-ray energies, photoelectrons could be emitted from other orbitals.)*

1. Why was Mg used as the source instead of the more typical Al source?

*The incident X-ray energies from an Al source are high enough energy that the photons would eject electrons from Ni.  By using a Mg source, photoelectrons are ejected from Fe (which has lower binding energies for 2p electrons) but not from Ni.  This helps alleviate interference from the Ni atoms that are present.*

1. Which spectra in this figure are considered “controls”? For each of those measured spectra, what are each of the experiments controlling?

*From the bottom up:*

*“As deposited, 0% Fe” - this spectrum was taken of the thin film after it had undergone rigorous removal of Fe as per the experimental conditions, reagents, and treatments described.  This spectrum demonstrates that the treatment did not result in the incorporation of Fe to a level detectable by XPS.*

*“300 CV cycles, purified KOH, 0% Fe” - this spectrum was taken following 300 cyclic voltammograms, which demonstrates that the CV process does not cause incorporation of Fe into the samples. This result is another indicator that Fe has been scrupulously removed from the samples and electrolyte.*

*“no V applied, 2% Fe” - this spectrum shows the peak size for a given amount of time (12 min.) that the thin film was exposed to Fe without an applied potential, to contrast with the spectrum above it which had an applied potential for the same amount of time.  This spectrum shows that 2% of the incorporated Fe comes from exposure of the film to Fe regardless of an applied potential; presumably the remaining 3% (5% total) observed in the next spectrum is due to the voltage.*

1. After accounting for background counts (dark current), what is the expected count ratio between the peak at 711 eV in the top spectrum and the spectrum immediately below it?

*Because the top spectrum corresponds to a Ni/Fe atomic ratio of 75:25 and the spectrum below it has Ni/Fe of 95:5, it would be expected that the top peak has 5x as many counts.  Counts are directly proportional to the number of photoelectrons which is directly proportional to the number of atoms.  Nice!*

2. Now consider Figure 1(b), the cyclic voltammogram. The figure includes five consecutive sweeps of one sample of electrocatalyst for the OER reaction.

1. Define the initial conditions for the experiment in Figure 1(b).  Why are the initial conditions of the Ni(OH)2 film important?

*Ni(OH)2 was deposited onto the electrode surface, and the deposited material was rigorously prepared to be Fe-free.  This is important because the authors are testing the OER for its dependence on having Fe species incorporated into the catalyst film.  By starting with an Fe-free catalyst they can evaluate what happens when it is cycled in the presence of low levels of Fe-contaminated electrolyte.*

1. The CV was scanned five times.  What do you notice that changes over the cycles?

*Changes:  the position of the OER current becomes more negative with each scan.  The current trace begins to increase sooner and more steeply with each scan.*

1. For the feature(s) that change over the cycles, what is happening with the system?

*As the system is cycled, the catalyst becomes more active and OER current is increased and the onset voltage decreases. This means the catalyst becomes more effective with each sweep.*

1. What do the authors propose to explain the change?

*The authors argue that Fe is incorporated into the Ni(OH)2/NiOOH film with each sweep because Fe is present (as an impurity) in the electrolyte. As Fe is incorporated, the catalyst becomes more active and the OER current increases. The absence of Fe in the as-deposited film and its increase over 5 CV cycles is shown in Figure 1(a). This supports their argument that Fe impurities in the electrolyte affect the Ni(OH)2/NiOOH film, causing its catalytic activity.*

3. Considering both the XPS data and the CV data together, why are they combined in Figure 1?

*Cycle 1 and 5 traces shown in the XPS and CV.  Fe incorporation shown with XPS increases from 0 to 5% over 5 cycles.  OER current increases from scan 1-5. The XPS data and CV scans show the correlation between the presence/absence of Fe in the films and the OER current changes.*